Some Chemical Aspects Relating to Arsenic Remedial Technologies

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The information which is summarized here originates mostly from publications by well known and established authors in the field, during their many years of research on this subject. Most of the material is mentioned only briefly, but will be found in a publications list which is available by e-mail from the author. Although there are many other excellent relevant references, the author has chosen the selected papers for their reliability and convenience, but they are not necessarily the earliest chronological references. There are many other statements here which originate from much unpublished work. This extended abstract is an abridged version of the paper (with the references) that is available by e-mail.

Introduction

The removal of arsenic from process solutions and effluents has been practiced by the mineral process industries for many years. Existing hydrometallurgical techniques are adequate for most present day product specifications but the stability of solid and liquid waste materials for long-term disposal or discharge will not meet the regulatory requirements of the future. The removal and disposal of arsenic from metallurgical process and effluent streams will become a greater problem as minerals with much higher arsenic content are processed in the future, and as regulations become more stringent. Disposal of stable residues will be critical, and the testing methods for assessing stability will need thorough revision.

The various unit processes that have been considered to deal with arsenic in hydrometallurgical processes include: oxidation-reduction, precipitation and thermal precipitation, coprecipitation, adsorption, electrolysis and cementation, solvent extraction, ion exchange, membrane separations, precipitate and ion flotation, and biological processing. These methods are not considered here, but are detailed in some of the references in the e-mail version of this paper. Here only precipitation, adsorption and cementation are considered, as these are the processes that are presently being more generally adopted, and need further investigation.

The aqueous solution chemistry of arsenic and the most common hydrometallurgical methods that have been applied commercially for arsenic removal, recovery, and disposal are only mentioned briefly here, as are some techniques which have been used only in the laboratory, and otherwise suggested as a means of eliminating or recovering arsenic from solution.

The aqueous solution chemistry of arsenic that relates to hydrometallurgical processes has been extensively covered in the literature, and the use of thermodynamic stability diagrams to describe the chemistry has been widely adopted. The important oxidation states of arsenic are -3, 0, +3, and +5, and all have been utilized in some way in hydrometallurgy. The removal of arsenic from solution has relied mostly on precipitation and adsorption processes and it has been considered that arsenic(V) is the oxidation state that leads to the most effective removal by precipitation since the simple metal arsenates generally have lower solubility than the arsenites, and also arsenate is more strongly adsorbed on certain substrates, but this is pH dependent. The general assumption that arsenic(V) is more easily removed from solution, even by adsorption, is not correct. Current work has identified other compounds and also the element (formed by either cementation or electrolysis) to be appropriate low solubility materials for effective removal of arsenic from solution. Arsenic complexation in solution has had little attention, and it seems that only complexes of arsenic(V) with iron(III) have been studied to any extent. Oxidation of arsenic(III) in solution to arsenic(V), and reduction of arsenic(V) to arsenic(III) have been investigated as

part of the overall chemistry relating to hydrometallurgy. Oxidants such as air and oxygen, chlorine and hypochlorite, hydrogen peroxide, permanganate, ozone, and SO_2/O_2 have been investigated, both with and without catalysts. Photochemical oxidation of arsenic(III) to arsenic(V) is a recent innovation. The removal of arsenic from gold process solutions has been of understandable interest over the years, and has perhaps been investigated more than for other hydrometallurgical processes.

Precipitation

The insolubility of certain inorganic arsenic(V) compounds is the basis of many hydrometallurgical arsenic removal processes, and the insoluble product is often a disposal material. The most common methods of removing arsenic from aqueous process streams are by precipitation as arsenic(III) sulfide, calcium arsenate, or ferric arsenate, but it has been shown that all of these materials are unstable under certain conditions and therefore not suitable for direct disposal to uncontained sites as they will produce leachate containing arsenic.

The sulfide As_2S_3 has its lowest solubility below pH=4, but that solubility is significantly higher than has been generally accepted. The sulfide is not usually the form that is disposed in residues as it is easily oxidized and increasingly soluble above pH=4. There have been unsuccessful attempts to use As_2S_3 in landfill in which acidic-anaerobic conditions are maintained, and also in cement cast admixes. Recent work on biological formation of arsenic sulfides may have an application in treating process residues, but containment of waste material remains a problem.

There are a number of calcium arsenates that can be precipitated from arsenic(V) solutions, by lime addition to high pH. Lime addition in excess can reduce arsenic concentrations in solution to <0.01 mg/L, but those calcium arsenates which are precipitated at pH>8 are not stable with respect to the CO_2 in the atmosphere which converts them into calcium carbonate, releasing arsenic to solution in balance with appropriate cations.

Arsenic(V) can be precipitated from aqueous solutions below about pH=2 with iron(III) to form ferric arsenate, $FeAsO_4.2H_2O$, which is white to very pale green in colour. At ambient precipitation temperatures the compound is very small in crystal particle size (<10nm) and is "2-Line X-ray amorphous", but these particles tend to agglomerate to about 100nm and the material is difficult to de-water by conventional operations. At temperatures above about $90^{\circ}C$ the precipitated compound is crystalline (>100nm) and has a solubility about 2 orders of magnitude lower than the amorphous material (this is a particle size effect). The "amorphous" ferric arsenate exhibits incongruent solubility at about pH=1 (where [As] is about 500 mg/L) and at higher pH will convert very slowly to an arsenic bearing ferrioxyhydroxide, which initially forms around the surfaces of the ferric arsenate tending to stabilize the material and colouring it yellow to brown. Crystalline ferric arsenate (*scorodite*) has an incongruent solubility point at about pH=2 and is comparatively slow to convert to the arsenic bearing ferrioxyhydroxide, and for material of larger crystal particle size this may take some years. Crystals of $FeAsO_4.2H_2O$ do not grow to appreciable size (greater than about 1 mm) as they have a relatively high positive surface potential up to the pH of the incongruent point. Ferric arsenate of either form is not thermodynamically stable in the neutral to high pH region (the rate of decomposition being related to particle size and solution composition, and being controlled by diffusion through both the reactants and the product layer). The materials may pass conventional leach tests (such as the TCLP) and are not suited for direct un-contained disposal, but perhaps would satisfy a "slow release criteria" if regulatory authorities would give this option its deserved consideration. Ferric arsenate is also not stable in alkaline cement cast admixes.

There are other metal arsenates, such as those of Fe(II), Zn(II), Cu(II) and Pb(II), which are less soluble and more stable in the neutral pH region than the calcium arsenates or ferric arsenate, but these have not been seriously considered as disposal forms. Iron(II) arsenate has particular interest as a low solubility material and this

compound has recently been the basis of a process developed and sucessfully demonstrated in a variety of applications. Barium(II) arsenate was proposed as being an extremely insoluble arsenate, but this was shown to be incorrect. More complex compounds, such as the apatite structured calcium phosphate-arsenate have recently been demonstrated to be of low solubility and of appropriate stability (including being stable to atmospheric CO_2) for disposal considerations. Ferric arsenite sulfate is also of recent interest and may prove to be useful in stabilizing arsenic(III). One of the most insoluble arsenic compounds is lead(II) chloroarsenate, $Pb_5(AsO_4)_3Cl$, (the mineral form being *mimetite*) which has been studied in detail.

Very little attention has been given to mixed oxidation state materials (both Fe(II)-Fe(III) and As(III)-As(V) combination compounds have been tentatively identified, and the author is presently involved in a comprehensive study of these systems. The Fe(II)-Fe(III) hydroxy sulfate, $Fe^{II}_4Fe^{III}_2(OH)_{12}SO_4.8H_2O$, (known as "green rust") incorporates arsenic into the structure at pH<7, and is worthy of further study.

Adsorption of Arsenic on Ferrihydrite

Over many years there has been much attention directed to the removal of arsenic from hydrometallurgical process solutions and waste waters by precipitation and coprecipitation with iron(III). At relatively high concentrations of iron(III) and arsenic(V) (> about 0.001m) and at low pH, the precipitation results in the formation of ferric arsenate, $FeAsO_4.2H_2O$, as previously mentioned. At lower concentrations of arsenic(V) and higher iron(III) concentrations (where Fe/As>1), the coprecipitation of arsenic with ferrioxihydroxide (*ferrihydrite*) which occurs is probably the most effective method of removal of arsenic from aqueous solutions, and leads to a solid phase which can be stable at least for a year or so. The solid coprecipitate has been referred to as "basic ferric arsenate", and in 1985 a controversy commenced, as to whether the coprecipitated material was in fact a compound of iron(III) and arsenic(V) or simply an adsorptive binding of arsenic with ferrioxyhydroxide (*ferrihydrite*). There was even at that stage sufficient evidence to support the latter contention, but the use of the term "basic ferric arsenate" still exists and formulae such as "$FeAsO_4.xFe(OH)_3$" are used.

A number of studies have indicated that various complexes are formed in the adsorption of As(V) on ferrihydrite. EXAFS studies on arsenic bearing ferrihydrite formed at pH>7, have shown that arsenic(V) is adsorbed to ferrihydrite as a strongly bonded inner-sphere complex with either monodentate or bidentate attachment. It has also been reported that monodentate attachment predominates near the optimal pH=4-5 for adsorption.

The adsorption of arsenic(III) on ferrihydrite has also been investigated, but the optimal adsorption in this case occurs at pH 8-9, and although it seems an efficient process there is no evidence that the adsorbed species is in fact arsenic(III). It may be that during the process, oxidation of arsenic(III) will occur at the surface with some ease, being balanced by the reduction of Fe(III) to Fe(II) in the ferrihydrite structure, as has been shown in preliminary experiments by the author. It is well known that Fe(II) substitution in ferrihydrite does occur. Currently there is an investigation of the adsorption of As(III)-As(V) mixtures on ferrihydrite. Very little attention has been given to the possibility of modifying the ferrihydrite structure to improve its adsorptive capacity for arsenic in solution. It is well known that many cations will incorporate into the *goethite* structure, and therefore possibly into a precursor ferrihydrite. The author is aware of current work investigating the coprecipitation of both Al(III) and Mn(III) with Fe(III) to form an aluminic ferrihydrite and a manganic ferrihydrite respectively. Both materials are showing considerably better capacity for arsenic adsorption. The control of potential is important in this adsorption process. The effective oxidation of As(III) by manganese substituted goethite has been studied by XANES spectroscopy, and the implications are obvious in relation to adsorption mechanisms. There is little work reported on the adsorption of arsenic from solutions initially below say 50 µg/kg. This region of concentration is presently of immediate interest in relation to drinking water, where US EPA announced a new standard of 5 ppb (5 µg/kg) for the maximum level allowed (January 2001). However the scheduled effective date for applying this new rule has been delayed from 23 March to 22 May 2001.

Many substrates, other than ferrioxihydroxide, have been investigated and used commercially for removing arsenic from solution by adsorption. Some of these have shown excellent adsorptive capacity, but here there is not the scope for any details. Of personal interest is "adsorption" on sulfide minerals and titanium oxyhydroxide.

Cementation

It is well known that iron and other metals will replace arsenic from solution to produce arsenic as the element or as an alloy. This method of removing arsenic from solution to levels <2 µg/kg has been demonstrated on ground water at a commercial site in California at a pilot scale of 1-5 US gallons per minute. Cementation has also been suggested, demonstrated, and may be appropriate, for the removal of arsenic from drinking water.

Testing for Long Term Stability
Testing methods for evaluating the stability of hazardous waste residues have been defined by the US EPA in several "Background Document for Toxicity Characteristic Leaching Procedure" publications. The test methods do not adequately assess the long term stability of arsenical residues. Improved test methods must be designed which also include a characterization of physical properties and chemical components (mineralogy) so that predictions of behavior can be made.

Thermodynamic Modelling
The stability of arsenic species can be characterized by their standard free energies of formation ($\ddot{A}_f G^0$). Many of the papers referenced in the e-mail version of this paper have free energy of formation data for arsenic species which have been invaluable to the author in producing thermodynamic stability diagrams to gain a better understanding of arsenic systems. None of the reputable thermodynamic databases have significant relevant data, but there are a number of publications where reasonable data can be obtained, and it is likely that these data will be evaluated and a compilation produced in the near future.

Conclusions
There have not been any significant and innovative improvements in the methods for removing arsenic from process and effluent solutions, or for stabilizing sludges and residues, in the last decade or so. The current needs to remove arsenic from drinking water it seems is now a world problem, and so that too must be addressed.

References
This paper is available with references from bobrobins@bigpond.com.au.

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OUTLINE:

BRIEF MENTION OF HYDROMETALLURGICAL UNIT PROCESSES

SOME DETAIL OF PRECIPITATION AND ADSORPTION PROCESSES

- PRECIPITATION OF ARSENIC SULFIDE As_2S_3
- PRECIPITATIOM OF CALCIUM ARSENATES $CaHAsO_4$ etc.
- PRECIPITATION OF FERRIC ARSENATE $FeAsO_4.2H_2O$
- PRECIPITATION OF OTHER INSOLUBLE COMPOUNDS
- ADSORPTION ON FERRIHYDRITE AND OTHER MATERIALS

THERMODYNAMIC MODELING & STABILITY TESTING

Arsenic Geochemistry: Overview of an Underhanded Element

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Arsenic is 38th in cosmic abundance but only about 52nd in earth and crustal abundance. The formation of the earth apparently discriminated against arsenic. In the ocean, however, it is 26th in abundance, suggesting accumulation in seawater over geologic time. Arsenic is preferentially concentrated in shales relative to other major rock types. Partitioning into shales reflects the strong adsorption tendency of arsenic for clay minerals. During high-temperature processes, arsenic can be expelled from sediments and volcanics and concentrated in the fluid phase, especially at low porosity. This phenomenon may explain high arsenic in hydrothermal fluids and their ore deposits.

The geochemical cycle of arsenic from magmatic-hydrothermal processes through weathering, sedimentation, and diagenesis transforms the element and produces an array of natural sources. Probably the single most abundant mineral source of arsenic is arsenian pyrite. Pyrite is ubiquitous in the earth's crust and arsenic has a strong affinity for the sulfur site in pyrite, substituting up to about 10wt. %. Arsenopyrite contains higher concentrations of arsenic (39-53%) but is a much rarer mineral. Other arsenic-rich minerals include orpiment, realgar, and enargite. Weathering of these minerals in oxidizing environments solubilizes arsenic as As^{III} and ultimately as As^V. Arsenate, or As^V, has a strong adsorption affinity for hydrated iron oxides and in oxidized sediments iron oxides can be a source of soluble arsenic if they undergo reductive dissolution during early diagenesis. Geothermal springs are commonly enriched in arsenic, containing 0.1-5 mg/L dissolved arsenic as both As^{III} and As^V.

Arsenic concentrations in ground waters can range from less than a few μg/L to tens or even hundreds of mg/L in locally contaminated environments. Both anthropogenic and natural sources for arsenic in ground waters occur in many locations world-wide. Natural sources cause or have caused poisoning of populations in India, Bangladesh, Chile, Argentina, Mexico, Taiwan, Mongolia, Japan, and China. Mining activities are responsible for arsenic poisoning in Thailand. Arsenic mass poisoning in Bangladesh is the largest known, affecting nearly 30 million people.

The primary source of industrial and commercial arsenic was arsenic trioxide, produced as a by-product of metal mining and processing. Stockpiles still exist and are releasing soluble arsenic to ground waters. Several arsenic insecticides, herbicides, dessicants, wood preservatives, animal feed additives, drugs, chemical weapons, and alloys were produced for many years and sites are contaminated from these industries and their applications. Roxarsone, an organic arsenical, is still widely used today to clean parasites out from the stomachs of pigs and poultry.

Arsenic in surface and ground waters occur dominantly as either arsenite, As(III), or arsenate, As(V). Reduction of arsenic can produce methylated forms of arsenic. Several microorganisms, including species of fungi, algae, and bacteria, catalyze the reduction of arsenic. Oxidation of As(III) is also catalyzed by microbes and it has been demonstrated that soluble As(III) and arsenic sulfide minerals such as arsenopyrite and orpiment can be catalytically oxidized to soluble As(V).